



D-20752-1

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Serial No.: 09/661,902

Group Art Unit: 1724

Inventors: Ding et al

Filed: 9/14/2000

Title: POLYIMIDE GAS SEPARATION
MEMBRANES

Examiner: Spitzer

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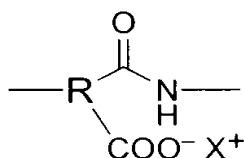
Mail Stop Non-fee Amendment
Commissioner for Patents
Alexandria, VA 22313-1450

Sir:

AMENDMENT

This is in response to the Office Action mailed April 9, 2003. A three-months extension of time is attached hereto in duplicate.

1. (Previously amended) A polyimide article formed from a polyamic acid salt precursory article by thermal or chemical imidization, wherein said polyamic acid salt precursory article is formed from a casting solution containing from 0.01% to 20 % by volume of tertiary amines or water, wherein said polyamic acid salt precursory article contains the following radicals:



wherein R is a substituted or unsubstituted aromatic, alicyclic, heterocyclic, or aliphatic radical; and

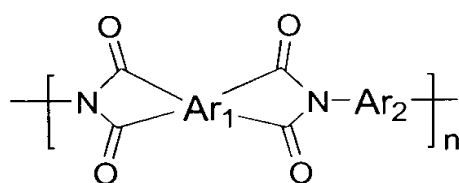
X is an ammonium ion, a phosphonium ion, a sulfonium ion, a protonated tertiary amine or a quaternary amine or a mixture thereof.

2. (Original) The polyimide article of claim 1, wherein said article is a fluid separation membrane.

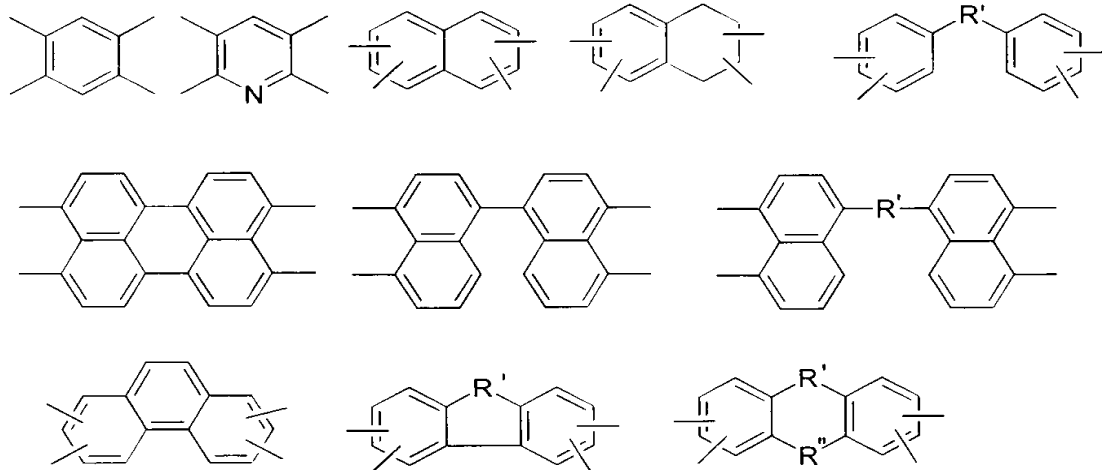
3. (Previously amended) The fluid separation membrane of claim 2 wherein said tertiary amine in said casting solution is the same as the protonated tertiary amine used to form the counter-ion X of said polyamic acid salt precursory article.

4. (Previously amended) The fluid separation membrane of claim 2 wherein said tertiary amine in said casting solution is different from the protonated tertiary amine used to form the counter-ion X of said polyamic acid salt precursory article.

5. (Original) The fluid separation membrane of claim 2 wherein the said polyimide is an aromatic polyimide of the following formula:

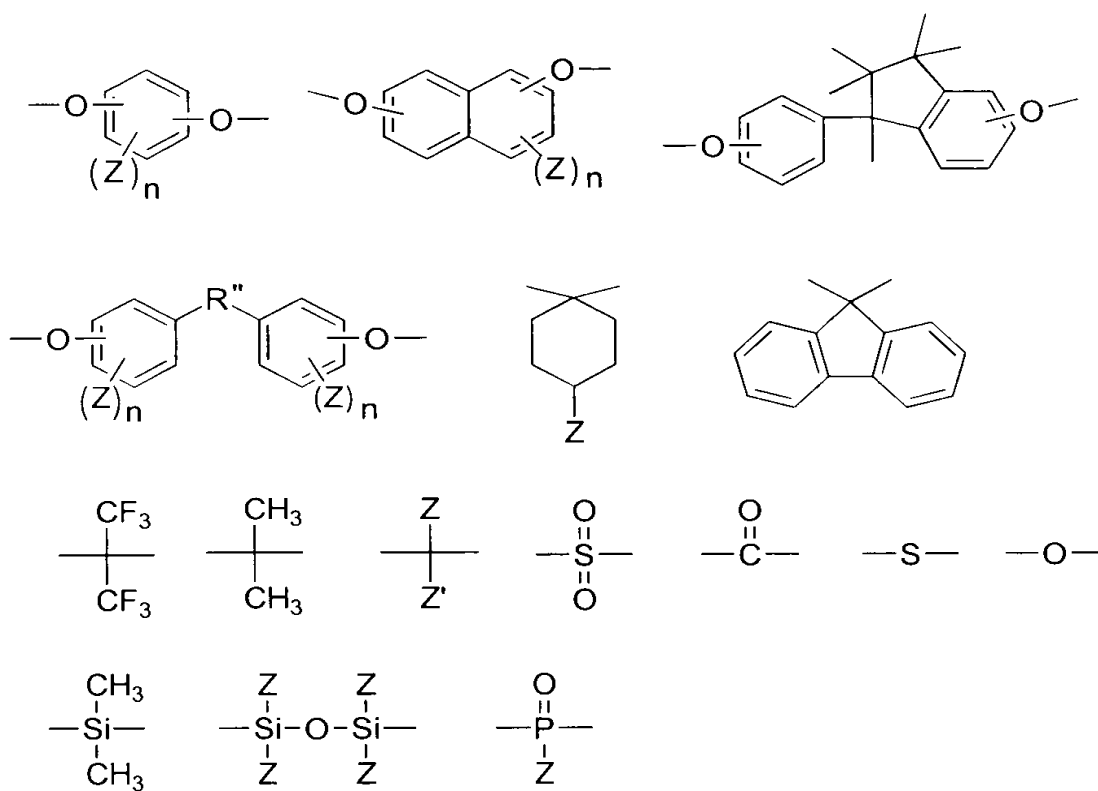


where Ar_1 is independently

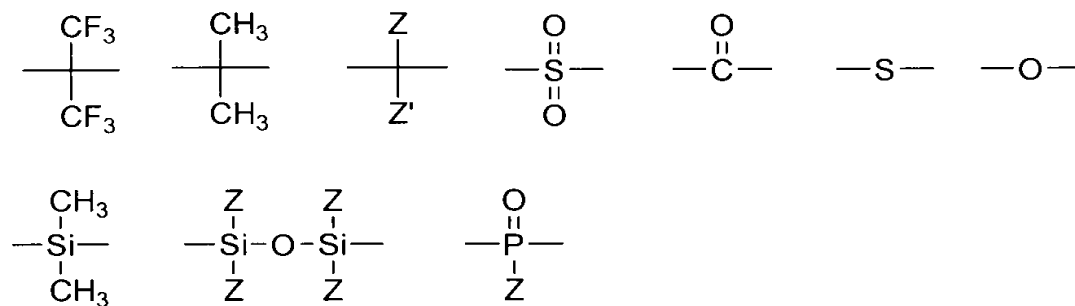


or mixtures thereof;

— R' — is

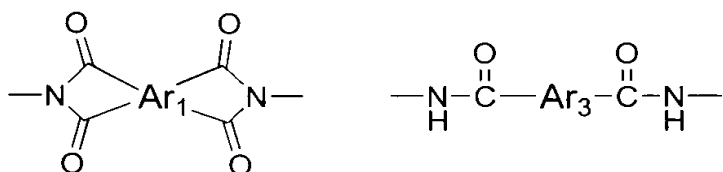
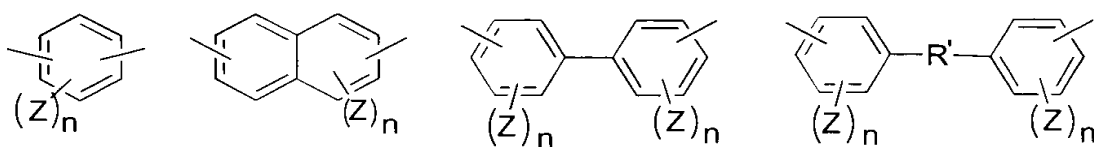


$-R''-$ is



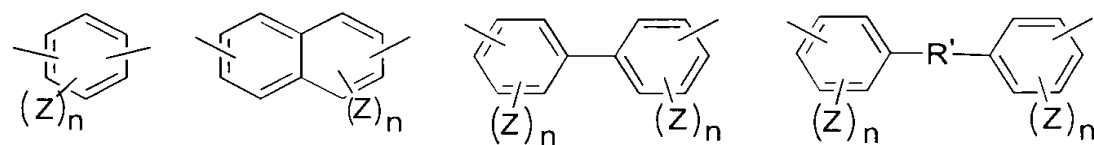
where $-Ar_2-$ is independently

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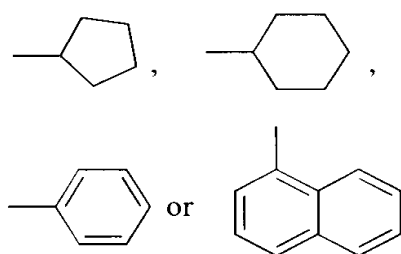
or mixtures thereof; where Ar1 is defined as above;

—Ar₃— is



Z and Z' are:

-H, -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, iso-propyl, iso-butyl, tert-butyl, -Br, -Cl, -F,
-NO₂, -CN



where n is between 1 to 4.

6. (Original) The fluid separation membrane of claim 2 wherein X is a protonated tertiary amine, tetraalkylammonium or ammonia.

7. (Previously amended) The fluid separation membrane of claim 6, wherein said protonated tertiary amine is protonated trimethylamine, protonated triethylamine, protonated tri-n-propylamine, protonated tri-n-butylamine, protonated tri-n-hexylamine or, protonated dimethylalkylamine.

8. (Previously amended) A polyimide fluid separation membrane wherein the polyimide membrane is a composite membrane formed by the following process: a) forming a coating solution of the polyamic acid salt polymer in a solvent system that contains from 0.01% to 20 % by volume of tertiary amine or water; b) applying said coating solution to a porous substrate to form a coated substrate; c) solidifying said coating solution by drying or by immersing said coated substrate into a non solvent; d) converting said coated substrate having the solidified coating into a final polyimide composite membrane by thermal or chemical treatment.

9. (Twice amended) The process of claim 8 wherein said solvent system ~~is comprised of~~ further contains ~~alcohols water or mixtures thereof~~ alcohols and water.

10. (Original) The process of claim 8 wherein said porous substrate is a hollow fiber.

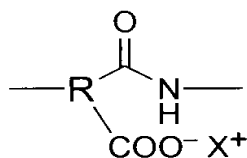
11. (Previously amended) The process of claim 8 wherein said porous substrate is formed from polysulfone, polyimide, polyamide, polyolefine, or polyetherimide.

12. (Original) The process of claim 8 wherein said thermal treatment is carried out at a temperature between 100 and 300 degrees centigrade.

13. (Original) The fluid separation membrane of claim 8 wherein said fluid is a gas mixture.

14. (Original) The fluid separation membrane of claim 8 wherein said polyimide is more than 50 % imidized.

15. (Previously amended) A polyimide article formed from a polyamic acid salt precursor article by thermal imidization, wherein said polyamic acid salt precursor article is formed from a casting solution containing a catalyst, and said polyamic acid salt precursor contains the following radicals:



wherein R is a substituted or unsubstituted aromatic, alicyclic, heterocyclic, or aliphatic radical; and

X is an ammonium ion, a phosphonium ion, a sulfonium ion, a protonated tertiary amine or a quaternary amine or a mixture thereof.

16. (Original) The polyimide article of claim 15, wherein said article is a polyimide fluid separation membrane.

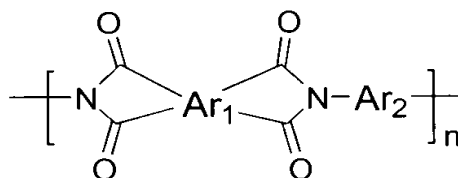
17. (Original) The membrane of claim 16 wherein said catalyst has an acid group that is neutralized with a tertiary amine.

18. (Previously amended) The polyimide fluid separation membrane of claim 16 wherein the temperature of said thermal imidization temperature is between 100 to 200 degrees Centigrade.

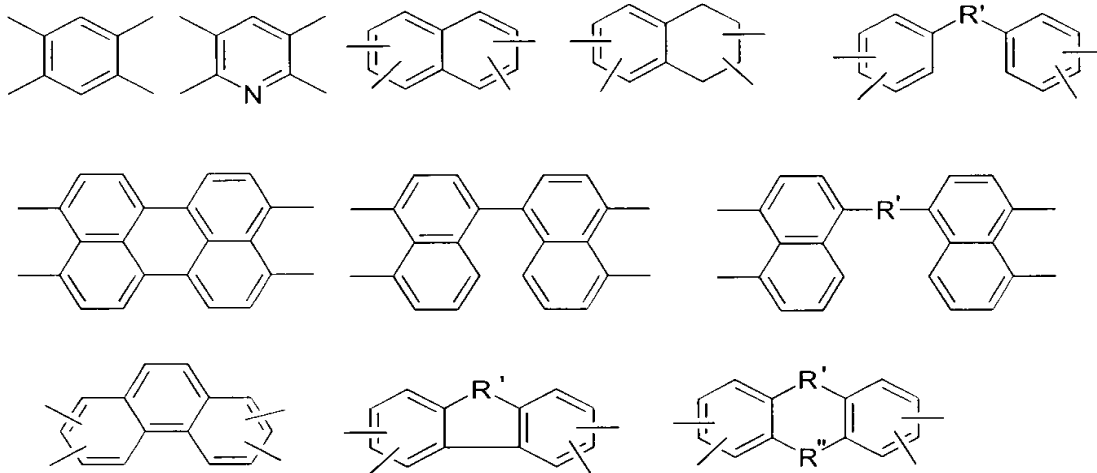
19. (Original) The membrane of claim 16 wherein said polyimide membrane is a composite membrane.

20. (Original) The membrane of claim 16 wherein said polyimide membrane is an asymmetric membrane.

21. (Original) The fluid separation membrane of claim 16 wherein said polyimide is an aromatic polyimide of the following formula:

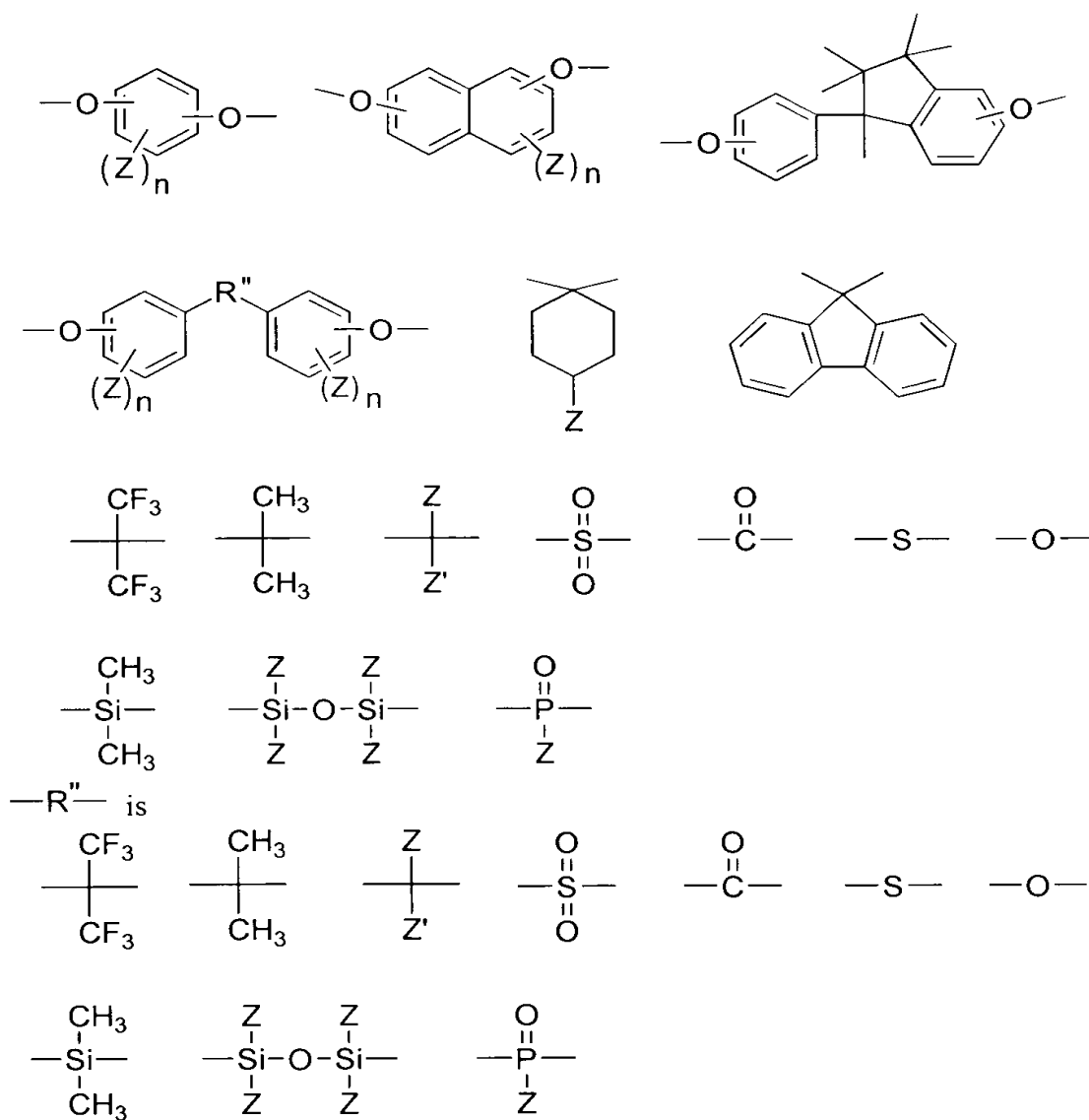


where Ar_1 is independently



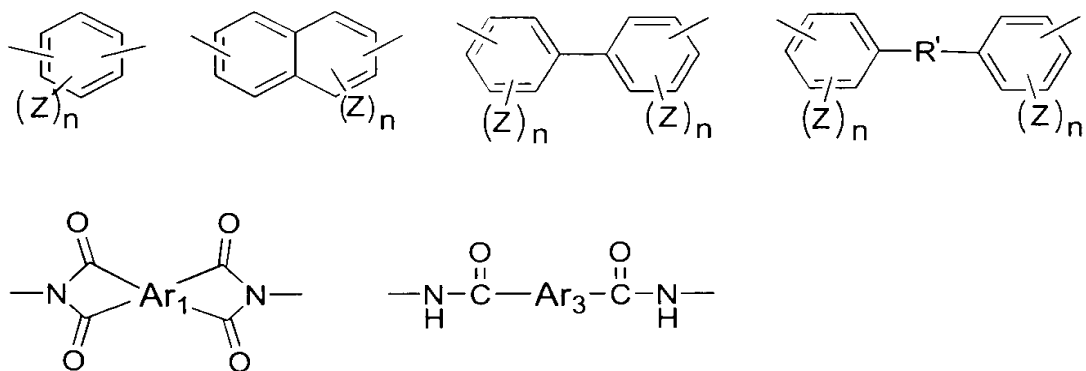
or mixtures thereof;

—R'— is

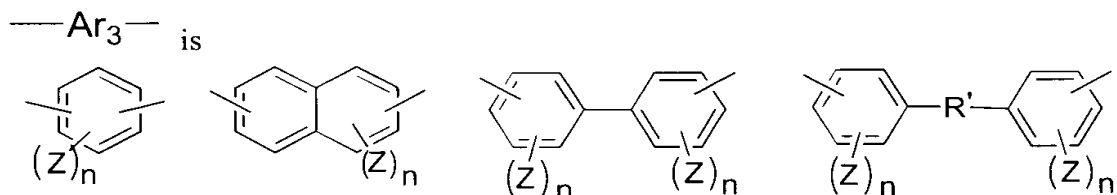


where $\text{—Ar}_2\text{—}$ is independently

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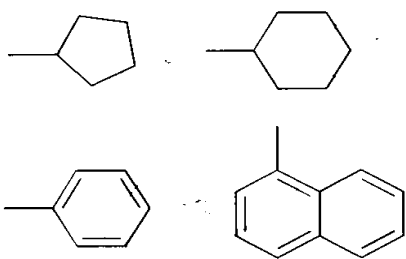


or mixtures thereof, where Ar_1 is defined as above;



Z and Z' are:

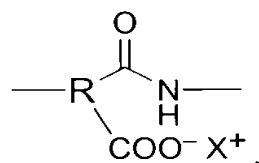
-H, -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, iso-propyl, iso-butyl, tert-butyl, -Br, -Cl, -F, -NO₂, -CN



where n is between 1 to 4.

22. (Original) The fluid separation membrane of claim 16 wherein the said polyamic acid salt has a counter ion that is a protonated tertiary amine, tetraalkylammonium or ammonia.

23. (Original) A polyimide fluid separation membrane formed from a polyamic acid salt precursor membrane by a chemical imidization process; said process comprising contacting said polyamic acid salt precursor membrane with a diluted dehydration agent in an inert solvent; wherein said polyamic acid salt precursor contains the following radicals:



wherein R is a substituted or unsubstituted aromatic, alicyclic, heterocyclic, or aliphatic radical; and

X is an ammonium ion, a phosphonium ion, a sulfonium ion, a protonated tertiary amine or a quaternary amine or a mixture thereof.

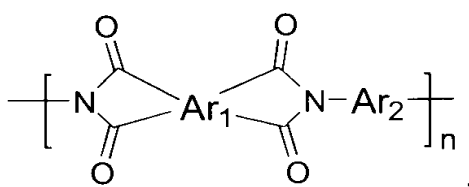
24. (Previously amended) The polyimide membrane of claim 23 wherein said inert solvent is hexane, cyclohexane, octane, pentane, ethyl ether, propyl ether, butyl ether, methyl t-butyl ether, petroleum ether, perfluorinated alkanes, perfluorinated alkyl ether, acetone or methyl ethyl ketone.

25. (Previously amended) The polyimide membrane of claim 23 wherein said diluted dehydration agent is an acid anhydride, acid chloride or an acetal.

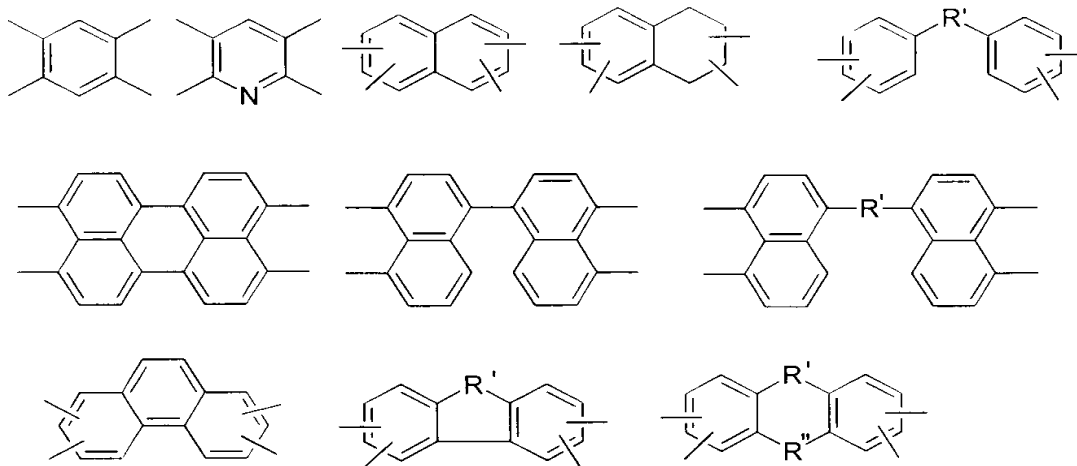
26. (Original) The polyimide membrane of claim 23 wherein the concentration of said dehydration agent in said inert solvent is from 0.1% to 5% by volume.

27. (Original) The fluid separation membrane of claim 23 wherein said polyimide is an aromatic polyimide of the following formula:

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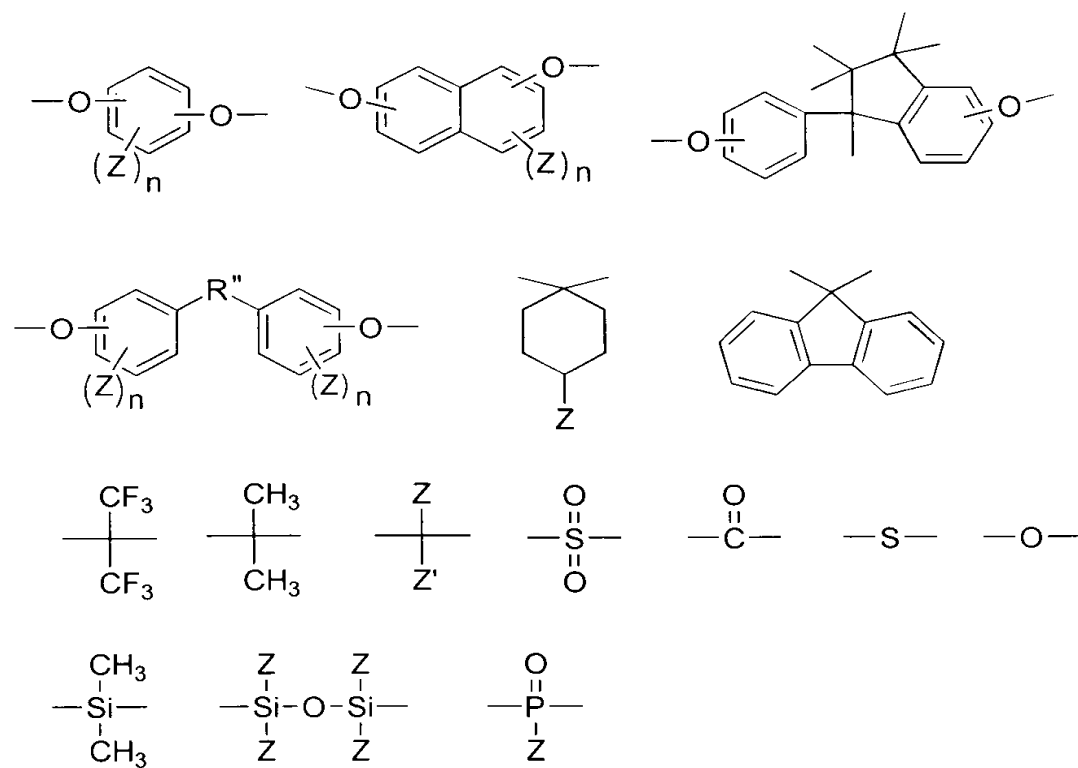


where Ar_1 is independently

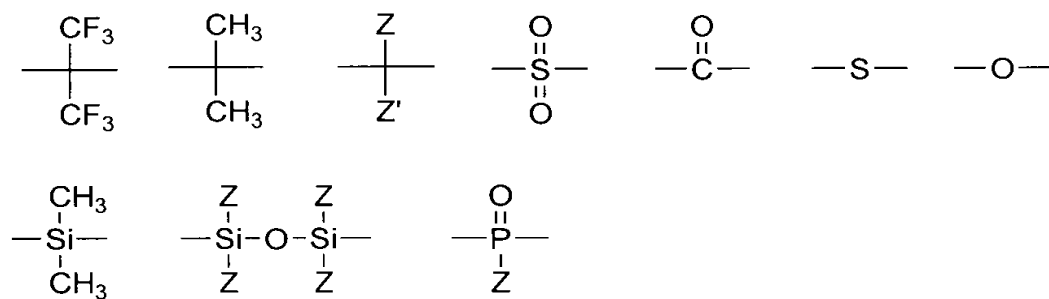


or mixtures thereof.

$\text{—R}'\text{—}$ is

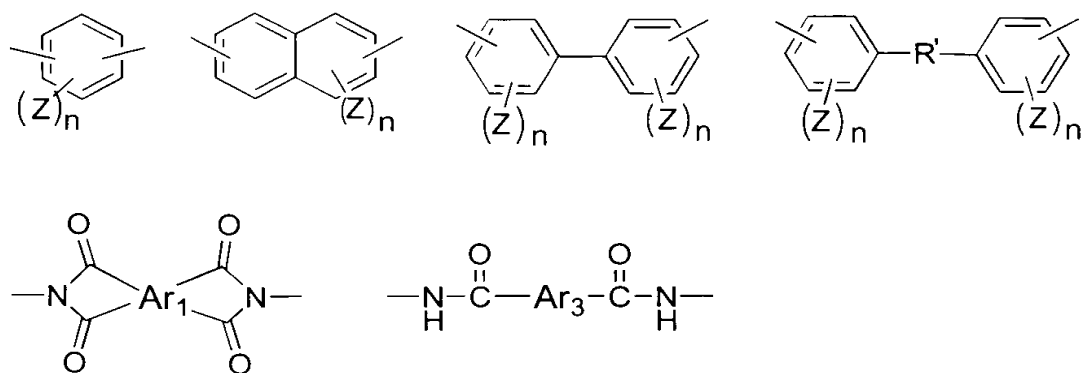


$\text{--R}''\text{--}$ is



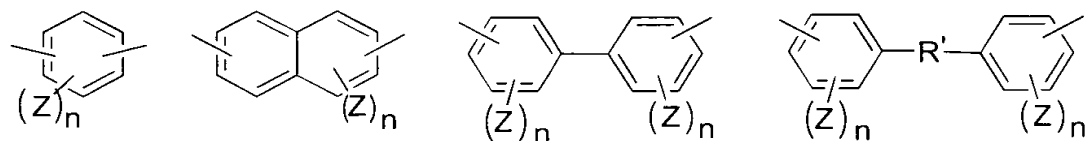
where $\text{--Ar}_2\text{--}$ is independently

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or mixtures thereof; where Ar_1 and Z are defined as above;

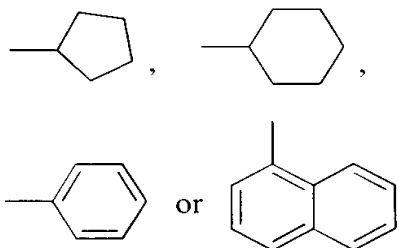
— Ar_3 — is



Z and Z' are:

-H, -CH₃, -CH₂CH₃, -CH₂CH₂CH₃, iso-propyl, iso-butyl, tert-butyl, -Br, -Cl, -F

-NO₂, -CN



where n is between 1 to 4.

28. (Previously amended) The fluid separation membrane of claim 23 wherein X is a protonated tertiary amine, tetraalkylammonium or ammonia.

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~~29. (Previously added) The process of claim 9, wherein said solvent system further contains up to twenty percent tertiary amines.~~

30. (Once amended) The process of claim ~~29~~8, wherein said solvent system further contains an imidization catalyst.